

Fluorescence Study Of Host-Guest Interaction Of 2-(4'-Pyridyl) Benzimidazole Derivative With Cucurbit[5]Uril At Two Different pH

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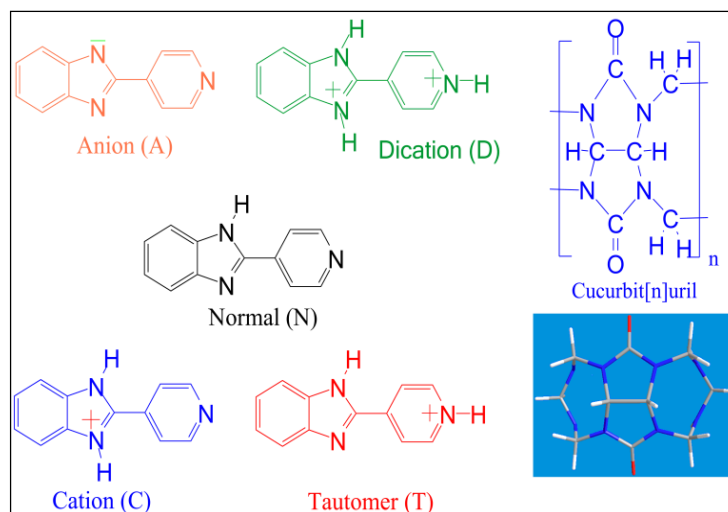
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Abstract

Supramolecular assembly effect on the excited state proton transfer of pyridyl benzimidazole derivatives has been explored by fluorescence and time-resolved measurements. This study is inspired by the earlier observation in 4-PBI in which the spectroscopic properties of the dye molecules is altered upon complexation and ESPT is enhanced due to formation of complex between host and guest molecules by non-covalent interactions in aqueous solution in cyclodextrins. The objective of the present study is to understand how the complicated acid base equilibria are affected in different size of supramolecular assembly upon complexation.

Introduction

Excited state intramolecular/intermolecular proton transfer (ESIPT) in hydrogen-bonded systems has been studied extensively. These processes are extremely fast and provide us valuable information related to energy and structure of molecule in a particular excited state. Proton and hydrogen transfer processes that have prospective applications in laser, and improvement of fluorescence devices based on sensing and therefore have created significant amount of curiosity.^{1,2,3,4,5} Benzimidazole derivatives have received considerable attention in this context. 2-(4'-pyridyl)benzimidazole (4-PBI) shown interesting acid-base behaviour due to presence of two nitrogen atom (Scheme 1).



Scheme 1: The different form of 4-PBI and the network of Cucurbit[n]uril

Different species that contribute to the ground and excited states of this molecule are the Neutral molecule **N**, monocation **C**, Tautomer **T**, dication **D**, and the anion **A**. The values of pK_{DT} and pK_{CN} are near in the ground and excited state. This indicates that the similar basicity of the benzimidazole nitrogen, N3 in both state. The high value of pK_{DC}^* and pK_{TN}^* is obtained in excited state, indicates that the big increase the basicity of pyridyl nitrogen.⁶

Table 1: The cavity size and the cavity shape of Cucurbit[5]uril

	CB[5]	
Outer diameter (nm)	a	1.31
Cavity (nm)	b	0.44
	c	0.24
	d	0.91
Cavity Volume (\AA^3)	--	82

It is exciting to identify whether this behaviour is altered in excited state upon complexation with Cucurbit[n]uril (CB[n]). So we investigate the photophysical behavior of 2-(4'-pyridyl)benzimidazole (4-PBI) in Cucurbit[5]uril (CB5). This study intends to understand the stabilization behaviour of the respective members of the Cucurbit[5]uril in aqueous solution with a possibility of two monocation to stabilize, both in the ground state and excited state as well. The chemical structures of CB5 are shown in Table 1. The CB[5] can encapsulate an entire metal cation and organometals with a

extraordinary binding attraction for positively charged organic guest molecules owing to the occurrence of carbonyl-laced portals. The inclusion complex has potential application in the field of separations, catalysis, sensors, and drug delivery and also in the creation in catenanes, and other novel molecular devices.⁷ In the current study, we have revealed the influence of CB5 on the modulation of proton-transfer processes of 4-PBI in the ground- and excited-state in solutions of two different pH in order to observe if the protonation-deprotonation stabilities including different species of 4-PBI are affected by complexation in macrocyclic hosts. Apart from the size, its variation of polarity has an impact on its interaction with the guest as well. It has a non-polar inside and polar portals towards the top and the bottom.

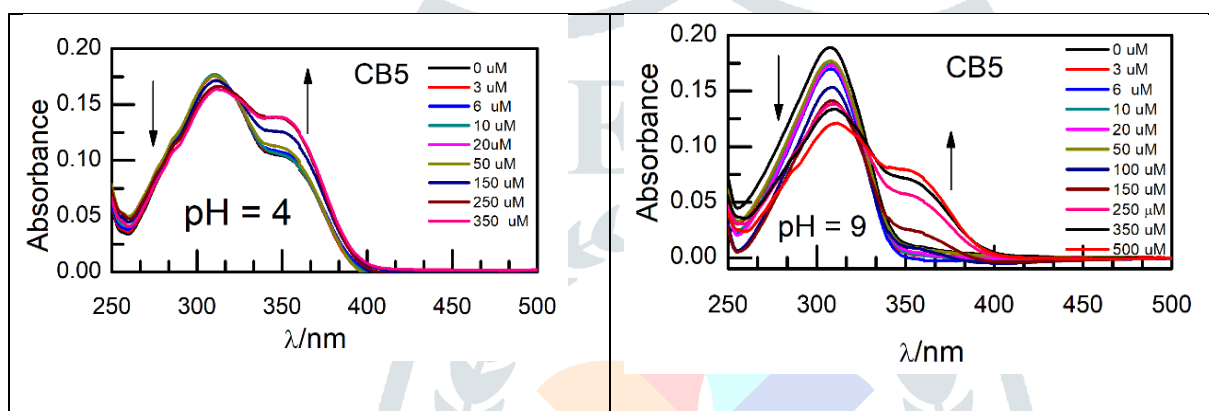


Figure 1. Absorption spectra of 4-PBI in Cucurbit[5]uril (CB5) at pH = 4 (Left) and pH = 9 (Right) in solutions at different concentration of CB5.

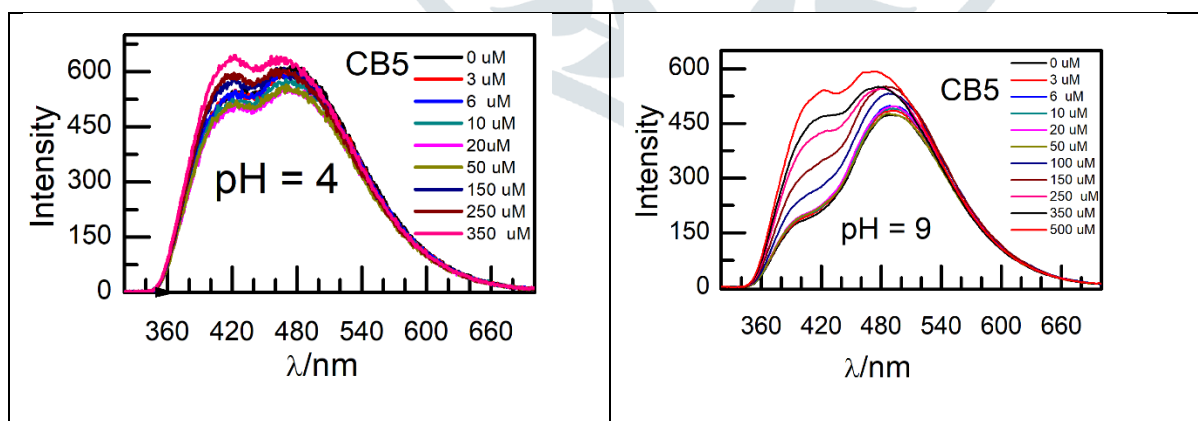


Figure 2. Fluorescence emission spectra of 4-PBI in Cucurbit[5]uril (CB5) at pH = 4 (Left) and pH = 9 (Right) in solutions at different concentration of CB5.

Results and Discussion

4-PBI absorption spectra in solution have been verified at different CB5 concentration at pH = 4 and pH = 9 and shown in figure 1 and 2. The Addition of CB5 at pH = 4 as well as pH = 9, is destabilized the N form of the molecule at the cost of the tautomer in ground state. This designates that the selectively stabilization of T and the complex formation of CB5 with 4-PBI in ground state. The fluorescence emission spectra of 4-PBI in CB5, the increase of the intensity at pH = 4 as well as pH = 9, the increment of the N* at pH = 9 is higher as compare to pH = 4 and the shape of the spectra is does not change appreciably. At pH 9, the peak at 380 nm is become red shifted and the band at 490 m is blue shifted. This indicates that the formation of complex with CB5 is more feasible for the C/N form of the guest molecule and the one form of the the dye is experience more hydrophobic environment as compare to other form (T).

Table 2. Time-based Characteristics of 4-PBI in CB5 at pH = 4.

[CB5]/ μM	$\lambda_{\text{em}} = 380 \text{ nm_pH } 4$					$\lambda_{\text{em}} = 490 \text{ nm_pH } 4$	
	τ_1/ns	a_1	τ_2/ns	a_2	χ^2	τ_1/ns	χ^2
0 μM	0.35	0.75	5.80	0.25	1.03	4.76	1.13
250 μM	0.37	0.60	5.63	0.40	1.05	4.86	1.09

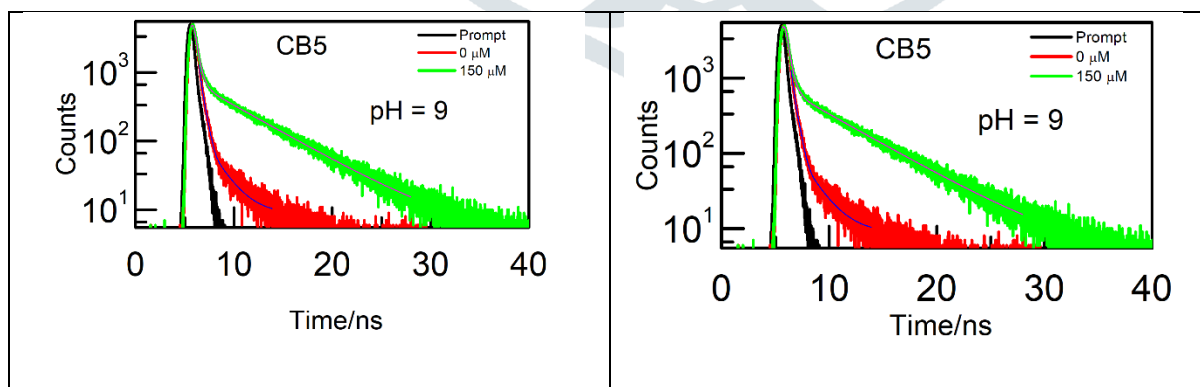


Figure 3. Lifetime parameter of 4-PBI in solutions at different concentration of CB5, $\lambda_{\text{em}} = 380 \text{ nm}$ (Left) and 490 nm (Right), $\lambda_{\text{ex}} = 295 \text{ nm}$ at pH = 9.

The fluorescence decays of the solution of the 4-PBI with CB5 and without at pH = 4 as well as pH = 9, have been recorded at $\lambda_{\text{ex}} = 295 \text{ nm}$, with emission wavelength at $\lambda_{\text{em}} = 380 \text{ nm}$ and $\lambda_{\text{em}} = 490 \text{ nm}$

and the lifetime is determined by fitting single- or bi exponential are listed in table 2 and 3. The fluorescence decay at pH 4, at $\lambda_{em}= 380$ nm and 295 nm excitation is biexponential with lifetime 0.20 ns (0.80) and 5.80 ns which corresponds to the normal form and C form of 4-PBI, respectively and at $\lambda_{em}= 490$ nm, the decay is single exponential with lifetime is 4.76 ns which correspond to T form of 4-PBI. Upon addition of CB5 the decays are biexponential with increasing smaller lifetime to 0.37 ns (0.60) and the decreasing the longer lifetime to 5.63 ns. This designates that the development of the complex with the normal form of the 4-PBI. The lifetime at 490 nm emission in presence of CB5 is 4.86 ns.

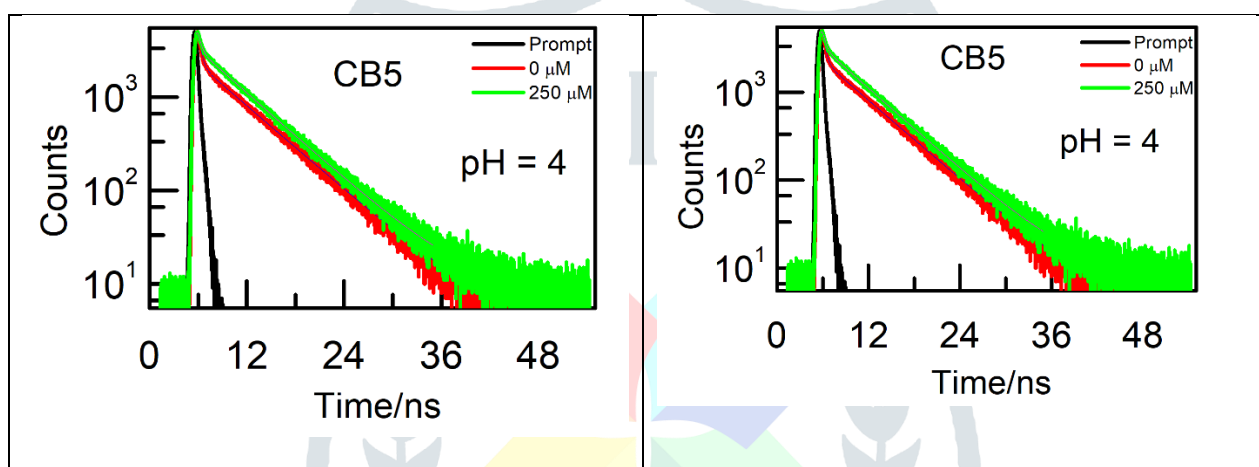


Figure 4. Fluorescence decay of 4-PBI in solutions at different concentration of CB5, $\lambda_{em} = 380$ nm (Left) and 490 nm (Right), $\lambda_{ex} = 295$ nm at pH = 4.

Table 3. Time-based Characteristics of 4-PBI in CB5 at pH =9.

$\lambda_{em} = 380$ nm_pH 9						$\lambda_{em} = 490$ nm_pH 9				
[CB5]/ μ M	τ_1 /ns	a_1	τ_2 /ns	a_2	χ^2	τ_1 /ns	-	-	-	χ^2
0 μ M	0.15	0.99	1.71	0.01	1.08	4.12	-	-	-	1.20
150 μ M	0.34	0.93	3.61	0.07	1.11	4.26	-	-	-	1.05
500 μ M	0.40	0.70	5.41	0.30	1.03	4.59	-	-	-	1.07

Conclusion

As we have seen from the spectroscopic study that the size of the CB5 is not appropriate to form the inclusion complexes and there is no change in the lifetime of 4-PBI, when CB5 is added. The changes observed in the absorption and fluorescence spectra is due the simple electrostatics interaction only. There is no evidence of the inclusion of the dye inside the CB5 cavity.

References

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